

DUROVITSKIY, A. K.

Electric Currents - Grounding; Dynamos

Operation of protective devices against ground short
circuit of generators. Elek. Sta., No. 1, 1952.
Gorensergo Inzh.

SO: Monthly List of Russian Accessions, Library of Congress, March 1952 ~~1953~~, Uncl.

1. DUBOVITSKIY, A. R.
2. USSR (600)
4. Dynamos
7. Operation of a differential, transverse protection of a generator during a double short circuit of the rotor armature to the ground. ^{Elek. sta.} 23 no. 12: 1952

9. Monthly List of Russian Accessions, Library of Congress, April 1953, Uncl.

DUBOVITSKIY, ABRAM MARCO
1957

DECEASED

see ILC

chemistry

TITLE: Radiochemical decomposition of AuCl₄ #

SOURCE: Kinetika i kataliz, v. 6, no. 5, 1965, 828-835

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$$\text{CrO}_4^{2-} \xrightarrow{\text{H}^+} \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{CrO}_3 + \text{H}_2\text{O}$$

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AFSOL 2886

UNCLASSIFIED Y5 223/0830

Author: G. M. Buben, N. Ya.; Dubovitskiy, A. V. Kiselev, G. R.

Reaction of irradiated ammonium perchlorate by the electron paramagnetic method

Journal: Kataliz, v. 5, no. 5, 1964, 821-824

Abstract: Ionizing irradiation, ammonium salt, perchlorate, electron paramagnetic radiation chemistry, chemical kinetics

The nature, accumulation, and recombination of paramagnetic centers under the action of ionizing radiation in pure ammonium perchlorate NH_4ClO_4 with additions of CaO , MnO_2 , $CaCO_3$, $Ca(OH)_2$, $CaCl_2$, $CaSO_4$, and KNO_3 (co-crystallized with NH_4ClO_4) were studied in the range 150-400°K by the electron paramagnetic resonance method. A correlation was found between the behavior of radicals in ligand and thermal decomposition of ammonium perchlorate NH_4ClO_4 .

UFG:7886

a good model (observed by the electron paramagnetic resonance) investigating typical properties and behavior of these particles in reactions. Orig. art. has: 3 figures, 1 table, 2 graphs.

Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics)

162

ENCL: 00

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OTHER: 004

DUBOVITSKIY, A.Ya. (Moskva); MILYUTIN, A.A. (Moskva)

Some optimum problems for linear systems. Avtom. i telemek. 24 no.12:
1616-1625 D '61. (MIRA 17:1)

DUBOVITSKIY, A. YA.

PA 246196

USSR/Mathematics - Measure Theory Mar/Apr 53

"Differentiable Representations of an n -Measure
Cube Into a k -Measure Cube," A.Ya. Dubovitskiy,
Vologda

"Matemat Sbornik" Vol 32 (74), No 2, pp 443-464

An extension of the results of A.S. Kronrod and
Ye.M. Landis (cf. "Sets of a 'Level' of Functions
of Many Variables," Dok Ak Nauk SSSR, Vol 58, No 7
(1947), 1269-1272) on zero measure of a set to the
case of projections of an n -dimensional cube C_n
into a k -dimensional cube C_k .

246196

DUBOVITSKIY, A.Ya. (Vologda)

Axiomatic construction of real numbers; teaching in pedagogical
institutes. Mat. proc. no. 2: 157-168 '57. (MIRA 11:7)

(Numbers, Theory of)

AUTHOR
TITLE

DUBOVITSKIY A.YA.

38-3-5/7

On the Structure of the Amounts of the Level of the Differentiable Images of an n-Dimensional Cube on a k-Dimensional Cube.

(O strukture mnozhestv urovnya differentsiruyemykh otobrazheniy n-mernogo kuba v k-merom kub-Russian)

PERIODICAL

Izvestia Akad.Nauk SSSR,Ser.Mat.,1957,Vol 21,Nr 3,pp 371-408 (U.S.S.R.)

ABSTRACT

The present paper studies the connection between the typical amount of the levels and the degree of the smoothness of a differentiable image. The determination of all solutions of a system of the type $u_1(x_1, \dots, x_n) = c_1, u_2(x_1, \dots, x_n) = c_2, \dots, u_k(x_1, \dots, x_n) = c_k$ is equivalent to the determination of the corresponding amounts of the level E_n . A definition of this conception is given. The case that any of the k values of the unknown solution, at least locally, are unique functions of the values of the remaining unknown quantity, is of special interest. The present paper furnishes a series of theorems which characterize the structure of a typical amount of the level of a smooth image. The results thus obtained are then used for study of a typical amount of the level of the differentiable functions of several invariables. The first chapter proves several auxiliary theorems to be used later. The second chapter then studies the connection between the degree of smoothness of the image and the structure of its typical levels. This chapter is divided into the following sections: The main

Card 1/2

On the Structure of the Amounts of the Level of the 38-3-5/7
Differentiable Images of an n -Dimensional Cube on a k -Dimensional
Cube.

theorem; an example for the impossibility of the attenuation of
the conditions of the theorem; the structure of the levels of the
differentiable images of the n -dimensional cube C_n onto the k -
dimensional cube C_k ; the amounts of the level of the functions of
several variables.

(No illustrations)

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|--------------|----------------------------------|
| ASSOCIATION | Not Given. |
| PRESENTED BY | ALEKSANDROV P.S., Academy Member |
| SUBMITTED | 7.5.1956 |
| AVAILABLE | Library of Congress. |
| Card 2/2 | |

AUTHOR: Dubovitskiy, A.Ya. SOV/38-22-5-7/10

TITLE: On the Points of Complete Degeneration of the Jacobian Matrix
(O tochkakh polnogo vyroshdeniya matritsy Yakobi)

PERIODICAL: Izvestiya Akademii nauk SSSR, Seriya matematicheskaya, 1958,
Vol 22, Nr 5, pp 705-716 (USSR)

ABSTRACT: Let U be the mapping of the domain $G \subset E^n$ into E^k given by the
 m times differentiable functions $u_i(x_1, \dots, x_n)$, $i=1, 2, \dots, k$.
The point $x \in G$ is called a point of the complete degeneration
of the Jacobian matrix if the rank of $\left\| \frac{\partial u_i}{\partial x_j} \right\|_x$ equals zero.
Let N be the set of points where that happens. The present paper
is devoted to the investigation of the structure of N .
The ray $x_0 x$ is called a semitangent of the set E if there exists
a sequence x_n of E so that $\lim_{n \rightarrow \infty} x_n = x_0$ and $\lim_{n \rightarrow \infty} \frac{\varphi(x_n, x_0 x)}{|x_n - x_0|} = 0$
The sum of all semitangents of E in x_0 is called the contingence
of E in x_0 . The contingence of E in x_0 is not greater than s if
it can be situated in a hyperplane, the dimension of which is $\leq s$.

Card 1/2

On the Points of Complete Degeneration of the Jacobian Matrix SOV/30-22-5-7/10

Let m_α denote the α -dimensional Hausdorff measure. E is called α -essential if $m_\alpha U(E) > 0$.

Principal theorem: Every B-set N , in each point of which the contigence is $\leq \omega \cdot m$, is ω -unessential, i.e. $m_\omega U(N) = 0$ (ω is an arbitrary positive number).

By an example it is shown that the assumptions of the theorem cannot be weakened.

There are 7 references, 5 of which are Soviet, and 2 American.

PRESENTED: by P.S.Aleksandrov, Academician

SUBMITTED: July 11, 1957

Card 2/2

DUBOVITSKIY, A.Ya.

Sets of points of given degeneration of a Jacobi matrix of
an infinitely differentiable mapping. Izv.AN SSSR.Ser.mat
26 no.4:489-494 J1-Ag '62. (MIRA 15:8)
(Topology)

DOV, TSKIY, A.Ya.; MILYUTIN, A.A.

Extreme problems with some limitations. Dokl. AN SSSR 149
no.4:759-762 Ap '63. (MIRA 16:3)

1. Institut khimicheskoy fiziki AN SSSR. Predstavleno akademikom
S.L.Sobolevym.

(Calculus of variations)

...skiy, A. Ya. (Moscow); Milutin, A. I.

...problem with restrictions

...matematiki i matematicheskogo fizicheskogo, no. 3,

...control }

...give a self-contained exposition of a general approach
...with restrictions, considering a number of problems
...which were not treated or only partially treated in [3].

~~...skiy, A. Ya. (Moscow); Milutin, A. I. (Moscow)~~
...teoriya optimal'nykh protsessov. V. I. ... Their
...consist of functional analytic generalizations of finite dimen-
...and minima under constraints. The last section of the book concerns
...the general form of a functional from a given cone. The book
...the most typical functionals and contains a large number of large
...examples and omitting proofs which add little to the understanding. They

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...ing a multidimensional variational problem. In conclusion we thank
... from the idea of writing this article. ... discussed
... basic aspects. We also thank G. G. Vilenkin for her help in the pro-
... this work." Orig. art. has: 41 lines, 1 page.

name

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12

OTHER: 00

Small variations in problems on an extremum with constraints

Doclady, v. 160, no. 1, 1965, 18 p.

quadratic polynomial, nonlinear system, function programming

Function-

Authors attended some of their own work (see, for example, DAN, 149, No. 1, 1961). In the present paper, the method was described. The authors consider the problem of finding higher-order approximations to the basic minimization problem. The relationships are accounted for between the problem is stated and the results. Second-order variation is introduced and the problem of V. A. Markov (1917) is taken as an illustrative example.

involving a linear constraint. The authors describe the resulting optimization problem. The authors also discuss the problem of finding higher-order approximations to the basic minimization problem. The authors also discuss the problem of finding higher-order approximations to the basic minimization problem.

minima, where $-1 < x < 1$, the problem is

the minimum of

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28

The mechanism of the ignition of a mixture of hydrogen and oxygen. P. 111.
Inventor: P. 111. (No. 1, 201, 210, 1912). By streaming an H_2 which
through a heated glass tube it obtained a flame only 4° hotter than the gas mist.
Furthermore, the tube in which the gas mist was burning could be cooled as much as 60°
below the ignition temp. without extinguishing the flame. This latter observation is
considered evidence against the hypothesis that the upper explosion is brought about by
breaking of reaction chains in the gas phase. P. 11. Forster ✓

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DUBOVITSKIY, E. I.

The question of the mechanism of the inflammation of mixtures of $H_2 + O_2$. P. Dubovitskiy. *J. Phys. Chem. (U. S. S. R.)* 3, 270-1 (1932).—See C. A. 26, 5730.

R. H. RATHMANN

250-55.6 METALLURGICAL LITERATURE CLASSIFICATION

BC

17-1

Ignition limits of oxygen-hydrogen mixtures. *J. Am. Chem. Soc.* (Acta Physicochim. U.R.S.S., 1933, 2, 761-774).—The reaction between stoichiometric proportions of H_2 and O_2 irradiated by a H_2 tube at pressures and temp. close to the ignition limits has been investigated. The limits of ignition are not determined by the surface. A decrease in reaction rate at high pressures in presence of A terminates that chain branching grows in consequence of increased probability of the triple collision $O + H_2 + M = H_2O + M$. The primary process in the reaction is $O_2 + H_2 = O^* + O$. The results obtained are combined with earlier data and interpreted through Semenzov's chain theory. T. G. P.

APPROVED FOR RELEASE: 08/25/2000

CIA-RDP86-00513R000411410005-5"

USSR/ Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry.
Catalysis

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Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11219

within a definite region, limited by upper and lower boundaries. The authors interpret the data obtained on the basis of chain theory, making the assumption that the intermediate product of PH_3 oxidation -- H_3PO_2 , possesses the property, analogously to NO_2 , of yielding an O atom to the molecule of the reducing agent, and undergoing thereafter oxidation by O_2 . Thus in the presence of CO the H_3PO_2 supplies active O centers that propagate the principal oxidation chain: $\text{O} + \text{PH}_3 \rightarrow \text{H}_3\text{PO}$; $\text{H}_3\text{PO} + \text{O}_2 = \text{H}_3\text{PO}_2 + \text{O}$, which indicates increased probability of a branching of PH_3 oxidation chains in the presence of CO.

AUTHORS: Korzhanov, A. G., Dubovitskiy, F. I. SCV/20-120-5-32/67

TITLE: The Quasi-Steady Course Taken by Explosion Reactions
(Kvazistatsionarnyy teplovoy rezhim prottekaniya vzryvnykh reaktsiy)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 5, pp.1068-1071
(USSR)

ABSTRACT: First the unsteady system of equations describing a thermal explosion and the pertinent initial conditions are given. The authors study, without loosing the general character of the final conclusions, the most simple type of a self-accelerating reaction, that is to say the auto-catalytic reaction of first order: $\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$, where η_0 denotes the criterion of autocatalicity, this quantity being basically small. ($10^{-1} - 10^{-3}$). The quasi-steady system of equations is written down. Only in a certain interval above the boundary of the explosion the reaction proceeds still in a quasi-steady manner. The expressions resulting from the solution of the system of equations for the critical conditions of the depth of the preliminary reaction, for the

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The Quasi-Steady Course Taken by Explosion Reactions SOV/20-120-5-39/67

period of induction, for the period of induction above the boundary of explosion, and for the course of the reaction with time are written down. The quasi-steady behavior can be considered as a limit case of the non-isothermal course of the reaction. In self-accelerating reactions it occurs even above the boundary of explosion. The width of the domain of the preliminary reaction of the explosion is dependent upon the degree of self acceleration. In reactions with normal kinetics the reaction is quasi-steady only below the boundary of the explosion after the maximum of heating. A formula is given for estimating the period of induction. The authors thank for valuable suggestions made by N. N. Semenov, Member, Academy of Sciences, USSR, and by Ya. B. Zel'dovich, Corresponding Member, Academy of Sciences, USSR. There are 3 figures and 4 references, 4 of which are Soviet.

PRESENTED: February 3, 1958, by V. N. Kondrat'yev, Member, Academy of Sciences, USSR

Card 2/9

2(1), 5(4)

AUTHORS:

SOV/20-121-4-26/54

Dubovitskiy, P. I., Manelis, G. B., Merzhanov, A. G.

TITLE:

The Formal-Kinetic Laws of the Thermal Decomposition of Explosive Substances in the Liquid Phase (Formal'no-kineticheskiye zakonomernosti termicheskogo razlozheniya vzryvchatykh veshchestv v zhidkoy faze)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 121, Nr 4, pp 668-670 (USSR)

ABSTRACT:

The investigation discussed in this paper takes into account also the variation of volume. In the overwhelming majority of cases the volume practically does not vary if two or more components are interchanged. In the first approximation it may therefore be assumed that the volume of the condensed phase is an additive function of the volumes of the non-reacted substance and of the condensed remainder. The volume of the liquid phase may be considered to be a linear function of the "degree of conversion" (glubina prevrashcheniya). If the volume is variable, the reaction of the n^{th} order satisfies the equation

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SOV/20-121-4-26/54

The Formal-Kinetic Laws of the Thermal Decomposition of Explosive Substances
in the Liquid Phase

$d\eta/dt = k - (1 - \eta)^n / (1 - \mu\eta)^{n-1}$. μ denotes the depth of the variation for a total decomposition. This reaction is reduced to the equation of a simple monomolecular reaction if the variation of the volume by the decomposition is sufficiently high. This implies that the reactions of the first order may proceed according to the monomolecular law and also according to the bimolecular law. Also the taking into account of the volume by the autocatalysis (which is caused by the final condensed products of decomposition) modifies the character of the kinetic curves. This case corresponds to the kinetic equation $d\eta/dt = k_1(1 - \eta) + (k_2\alpha(1 - \mu)\eta(1 - \eta)) / (1 - \mu\eta)$

where α denotes the share of the catalyzer in the condensed remainder. For $\mu = 0$, the last equation is reduced to the classical equation of autocatalysis. A diagram shows the calculated dependence of the reaction velocity on the depth of conversion for various values of μ . The maximal velocity and the corresponding depth of conversion η_{maximum} depend in a high degree on the value of μ . A formula for η_{max} is given. The experimental data found by the decomposition of

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The Formal-Kinetic Laws of the Thermal Decomposition of Explosive Substances
in the Liquid Phase

SOV/20-121-4-26/54

various substances in the liquid phase may be described sufficiently well by the equations deduced in this paper. There are 3 figures and 3 references, 2 of which are Soviet.

PRESENTED: April 4, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: March 8, 1958

Card 3/3

2(5)

SOV/20-124-2-34/71

AUTHORS: Merzhanov, A. G., Dubovitskiy, F. I.

TITLE: On the Theory of the Thermal Explosion of Condensed Explosives
(O teorii teplovogo varyva kondensirovannykh vv)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 2, pp 362-365
(USSR)

ABSTRACT: The authors first give a report on several previous papers dealing with this subject. The present paper deals with a more general theory which takes into account the removal of a part of the reaction products from the reaction volume. According to this theory for liquid explosives, all the main characteristics of the thermal explosion can be calculated: the critical condition, the depth of pre-explosion decomposition, and the period of induction. The removal of the gaseous products from the reaction volume is assumed to be a quasi-equilibrium process; this assumption is justified in the case of low rates of gas liberation. An expression is given for the rate of conductive heat transfer. The authors then give the system of equations for the thermal explosion. The removal of the gaseous product exercises a considerable influence upon the thermal ex-

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SOV/20-124-2-34/71

On the Theory of the Thermal Explosion of Condensed Explosives

plosion if the depth of the explosion reaction is comparatively great. The authors then investigate the simplest case among such reactions, viz. the autocatalytic reactions of the first order. Some characteristics of the thermal explosion can be calculated according to the steady theory of Frank-Kamenetskiy. Finally, the equation of thermal balance is given for the convective heat transfer. The expressions for the characteristics of thermal explosion can be deduced from the solution of a quasi-steady system. A diagram shows the results of some calculations. There are 1 figure and 5 Soviet references.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences, USSR)

PRESENTED: September 9, 1958, by M. N. Semenov, Academician

SUBMITTED: June 4, 1958

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5(4), 2(1)

SOV/20-126-4-34/62

AUTHORS:

Manelis, G. B., Dubovitskiy, P. I.

TITLE:

Thermal Decomposition of Explosives Below the Melting Point
(Termicheskoye razlozheniye vzryvchatykh veshchestv nize
temperatury plavleniya)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 4, pp 813-816
(USSR)

ABSTRACT:

The present paper deals with various cases of decomposition of solid explosives, thus taking the occurrence of a liquid phase into consideration. Assuming that the solid explosive is soluble in the reaction products and that a thermodynamic equilibrium between solid and liquid phases appears, the ratio a of the concentration $C_{B_{fl}}$ of the initial substance to the concentration $C_{A_{fl}}$ of the reaction products in liquid phase at constant temperature is a constant, which is independent of the progress of the reaction as long as a solid phase is still existent: $a = C_{B_{fl}} / C_{A_{fl}}$. If the decomposition in the solid phase

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SOV/20-126-4-34/62

Thermal Decomposition of Explosives Below the Melting Point

(index f) and in the liquid phase (index fl) are reactions of the first order, the following formula may be derived for the total rate of the reaction:

$$-\frac{dB}{dt} = \frac{1}{1-\mu} \frac{dA}{dt} = k_1 C_{B_f} v_f + k_2 C_{B_{fl}} v_{fl} = k_1 B_f + k_2 B_{fl}, \text{ whereby } \mu$$

holds for the change of volume at complete decomposition:

$$\mu = \frac{v_{\text{end}} - v_{\text{beginning}}}{v_{\text{end}}}. v_f \text{ and } v_{fl} \text{ denote the volumes of the}$$

solid and liquid phase, respectively. The connection between the reaction rate and the respective state η of the reaction

$$\left(\eta = \frac{B_0 - B}{B_0} = \frac{A}{A_0} \right) \text{ is expressed by the following equation:}$$

$$\frac{d\eta}{dt} = k_1(1-\eta) - k_1 a(1-\mu)\eta + k_2 a(1-\mu)\eta = k_1 + [a(1-\mu)(k_2 - k_1) - k_1]\eta. \quad (1)$$

If $a(1-\mu)(k_2 - k_1) - k_1 = k_m$ is used, this equation is simplified

$$\text{as follows: } \frac{d\eta}{dt} = k_1 + k_m \eta. \quad (1a) \text{ If the condensed products of}$$

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Thermal Decomposition of Explosives Below the Melting Point

SOV/20-126-4-34/62

the reaction act as catalysts for the decomposition, the following equation is found for the reaction rate until complete decomposition of the initial substance occurs:

$$\frac{d\eta}{dt} = k_1 + \underbrace{\left[k_2 a(1-\mu) + \frac{k_3 \alpha(1-\mu)a}{1+a} - k_1 a(1-\mu) - k_1 \right]}_{= k'_m} \eta \quad (4)$$

α = share of the catalyst in condensed products. k'_m is only dependent on temperature. Therefore $\frac{d\eta}{dt} = k_1 + k'_m \eta$ (4a) is obtained. This equation is distinguished from equation (1a) only by the value of k'_m . The influence of admixtures of chemically inert substances which can increase the decomposition rate of the explosive by converting part of the explosive into liquid form, deserves particular interest. This case occurs when the temperature of the respective eutectic of explosive and admixture is below the experimental temperature. In this case the following equation is found for the reaction rate as a function of η :

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Thermal Decomposition of Explosives Below the Melting Point SOV/20-126-4-34/62

$$\frac{dy}{dt} = k_1 + (k_2 - k_1) \frac{T}{B_0} a + \underbrace{[(1-\mu)a(k_2 - k_1) - k_1]}_{k_m} \eta \quad (6)$$

$T \dots$ inert admixture

If the solid phase has completely solved in the reaction products, the course of reaction changes in all cases investigated. The connection between the reaction rate and the respective state of reaction (η) was computed according to the equations (1) (for $k_1=1$, $k_2=100$, $\mu=0.9$), (4) (for $k_1=1$, $k_2=20$, $k_3=100$, $\mu=0.9$), and (6) (for $k_1=1$, $k_2=100$, $\mu=0.9$). The results are graphically described in 3 figures. More complicated cases can occur in real systems conditioned by a more complicated mechanism of chemical decomposition. There are 3 figures and 4 references, 1 of which is Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute for Chemical Physics of the Academy of Sciences, USSR)

PRESENTED: January 16, 1959, by V. N. Kondrat'yev, Academician

SUBMITTED: December 29, 1958

Card 4/4

DUBOVITSKIY, A. G.
F. I.

5(4) 5.1300(A), 5.4700

66435

AUTHORS: Mershanov, A. G., Abramov, V. G., SOV/20-128-6-40/63
Dubovitskiy, F. I.

TITLE: Critical Conditions for the Thermal Explosion of Tetryl

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1238 - 1241
(USSR)

ABSTRACT: The processes taking place in the explosion caused by heating molten tetryl were investigated experimentally. Figure 1 shows the experiment apparatus. Hot glycerol served as heat carrier. The temperature was measured by means of a thermocouple and recorded by a potentiometer of the type EPP-09. The critical conditions of the explosion caused by heating the material, i.e. the relationship between temperature and the dimensions and constants of the explosive characteristic of the transition from the non-explosive desintegration to the explosive one, were determined. It proved possible to stop the reaction at any time by quickly replacing hot by cold glycerol. Table 1 lists the experimental data, which permit the following conclusions: The experimental value of the critical temperature T_{cr} lies between the values found when assuming purely conductive and purely

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Critical Conditions for the Thermal Explosion of Tetryl SOV/20-128-6-40/63

convective heat transfers. Thus under experimental conditions a combined heat transfer took place. Observations by means of the television apparatus PTU-OM proved that the convection is due to the gas bubbles formed during the decomposition. This also results in a considerable increase in the initial heating over the value calculated according to N. N. Semenov's theory (Ref 5). The dependence of the induction period under critical conditions on the temperature may be represented by the equation $t_{cr} = 10^{-21.5} \cdot 49000/RT$ sec. The degree of decomposition found experimentally before the explosion set in lies in the vicinity of the calculated theoretical value of 0.49. The explosions exhibited a "soft" character in all experiments, and no impact wave formed. The influence found of the gaseous decomposition products upon the heat transfer is believed to hold for all liquid or molten explosives. There are 4 figures, 1 table, and 5 Soviet references.

PRESENTED: June 1, 1959, by V. N. Kondrat'yev, Academician

SUBMITTED: May 28, 1959
Card 2/2

5(4)

SOV/20-129-1-42/64

AUTHORS: Merzhanov, A. G., Dubovitskiy, F. I.

TITLE: On the Theory of Steady Burning of Powder

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 1, pp 153-156 (USSR)

ABSTRACT: Ya. B. Zel'dovich (Ref 1) set up equations for the calculation of the burning of the solid phase of powder from the characteristics of the gas phase. The present paper investigates the burning of powder as regards to the processes in the solid phase. The dependences between the temperature distribution in the powder, rate of burning, thermokinetic characteristics, processes going on in the solid phase, and of the heat flow entering from the gas phase are derived. In formulating the set of equations the experimental results by P. F. Pokhil (Ref 2) were taken into consideration, according to which the sum of the processes proceeding in the solid phase of the powder is exothermic. The set of equations is transformed to the nondimensional form by applying D. A. Frank-Kamenetskiy's rules (Ref 3). The authors give an approximate solution, arriving at the formula by O. I. Leypunskiy (Ref 5) for the heat reserve and the thickness of

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On the Theory of Steady Burning of Powder

SOV/20-129-1-42/64

the heated layer. Calculations based on the equations given and on data by Samsonov on pyroxilin powder are carried out (Fig 2, Table 2). There are 2 figures, 2 tables, and 6 Soviet references.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

PRESENTED: June 13, 1959, by M. N. Semenov, Academician

SUBMITTED: June 10, 1959



Card 2/2

Dubovitskiy, F.I.

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AUTHORS: Dubovitskiy, F. I. Barsykin, V. V., Merzhanov, A. G.

TITLE: Thermal Explosion of Dinitroxydiethylnitramine Under Conditions of Purely Convective Heat Transfer, *λ*

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 6, pp.1124-1126

TEXT: A method of studying the thermal explosion of liquid and molten explosives in purely convective heat transfer has been developed. In the tests, the method previously described by the authors (Ref. 1) for determining the critical conditions of thermal explosion was used, a device for mixing the substances (Fig. 1) being used in addition. This mixer was used for examining the critical conditions of the thermal explosion of dinitroxydiethylnitramine. The experimental results were compared with data calculated from N. N. Semenov's formula (Refs. 8,9), and good agreement was noted. There are 1 figure, 1 table, and 9 references: 5 Soviet, 3 Canadian, and 1 German. *X*

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Instr. Chem Physics AS USSR.

Dubovitskiy, F. I.

81937

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AUTHORS:

Dubovitskiy, F. I., Rubtsov, Yu. I., Barzykin, V. V.,
Manelis, G. B.

TITLE:

Kinetics of the Thermal Decomposition of Dinitroxydiethyl-
nitramine

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 6, pp. 1126-1128

TEXT: The kinetics of the thermal decomposition of dinitroxydiethyl-
nitramine is investigated here by three different methods: the evolution
of gas, the change of weight, and the evolution of heat. When studying
the kinetics on the basis of the evolution of gas, the same method as
earlier (Ref. 5) was used. The curves of the rate of heat evolution are
graphically illustrated in Fig. 1, and the temperature dependence of the
reaction rate constants in Fig. 2. The values obtained for the reaction
heat of the thermal decomposition of dinitroxydiethylnitramine are
tabulated. As may be seen from the Table, the thermal effect of the

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AUTHORS: Dubovitskiy, F. I., Rubtsov, Yu. I., and Manelis, G. B.

TITLE: Kinetics of Heat Evolution in the Thermal Decomposition of
Tetryl

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 10, pp. 1763-1766

TEXT: Since there are no experimental data available on the amount of heat resulting from thermal decomposition of explosives, as well as on the kinetics of heat evolution during the decomposition, the authors investigated the kinetics of heat evolution in the thermal decomposition of tetryl with a differential self-regulating calorimeter (Ref. 1). The determinations were made for the temperature range 130°-155°C, with the weighed portion being such as to permit the decomposition to be regarded as isothermal. As is shown by the curves (Fig. 1) representing the rate of heat evolution, the tetryl decomposition has a self-accelerating character. Table 1 gives the amounts of heat resulting from thermal

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Kinetics of Heat Evolution in the Thermal
Decomposition of Tetryl

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B015/B064

decomposition for the temperature range investigated; the mean value is 341 cal/g. The reaction kinetics of tetryl decomposition is described by an equation (2) of autocatalysis of the first order which takes account of the volume change occurring in the course of the reaction. The kinetic constants (Table 2) were determined from equation (2), and the values of the activation energies and the factors of the exponential functions from the temperature function of the rate constants. The kinetic constants obtained from heat evolution, on the one hand, and the weight loss, on the other, were found to be the same. There are 3 figures, 2 tables, and 4 references: 3 Soviet and 1 British.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: June 6, 1959

Card 2/2

87170

S/062/60/000/012/014/020
B013/B054

11.8300

AUTHOR: Dubovitskiy, E. I.

TITLE: Combustion of Secondary Explosives Under High Pressure
of Up to 1000 kg/cm²

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, 1960, No. 12, pp. 2334-2336

TEXT: In the present paper, the author reports on the continuation of his studies concerning the effect of high pressures on the combustion of explosives. He observed the combustion of Hexogen (cyclotrimethylene dinitramine) and Ten (pentaerythrite tetranitrite) in nitrogen medium at pressures of up to 1000 kg/cm². Apparatus were developed for these studies, in which experiments could be made at a steady gas pressure of up to 2000 kg/cm². The bombs were equipped with oblong or round windows for photographing the process. Besides, they were equipped with a sufficient number of entrances for thermocouples. A special feature was their large interior volume (5-10 l) which permits, at high initial pressures, the pressure increase due to gas formation during combustion to be reduced

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Combustion of Secondary Explosives Under
High Pressure of Up to 1000 kg/cm²

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S/062/60/000/012/014/020
B013/B054

to a minimum. Fig. 1 shows such a bomb for a constant pressure of 500 kg/cm² with an oblong window; type SA-500 (BD-500). The rate of combustion was determined from the time of luminescence recorded by a film on a rotating drum. Hexogen and Ten were pressed at 2700 kg/cm² into explosive charges weighing 4 g, 7-8 mm high, and 6.2 mm in diameter. These explosives do not burn at normal pressure. On the basis of observations (Fig. 2), the author derived an empirical equation for the rate of combustion between 1-900 kg/cm². The first term of the equation describes the steady combustion process at low pressures, the second term the unstable process at high pressures, resulting in an explosion when the pressure attains a certain magnitude. On the basis of these studies, it can be assumed that combustion takes place in the gaseous phase. The latter consists mainly of products of incomplete chemical decomposition, both above the burning surface and inside the explosive charge. In both cases, combustion proceeds at various velocities which depend to a different degree on the external pressure. Combustion above the burning surface naturally takes place at low pressures. At a pressure increase, combustion is shifted into the pores of the explosive charge, and proceeds just as in gas forming on the decomposition of the explosive above a

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Combustion of Secondary Explosives Under
High Pressure of Up to 1000 kg/cm²

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large branched surface. Owing to a poor gas escape, an unstable combustion state develops inside the explosive charge, which is accompanied by an explosion or detonation. It follows that, at less dense charges, the transition from slow to faster combustion rates at high pressure proceeds much more quickly. Fig. 3 shows the dependence $U = f(p)$ at differently compressed charges. Ya. B. Zel'dovich is mentioned. There are 3 figures and 7 Soviet references.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: April 16, 1960

Card 3/3

04628

3/076/60/034/010/008/022
B015/B064

H. 8200

AUTHORS: Merzhanov, A. G., and Dubovitskiy, F. I.

TITLE: The Quasi-steady Theory of Thermal Explosion of Self-
accelerating Reactions //

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 10,
pp. 2235-2244

TEXT: The papers by N. M. Semenov (Ref. 1), D. A. Frank-Kamenetskiy (Ref. 2), and O. M. Todes (Ref. 3) are to be regarded as the fundamental publications on thermal explosion. Subject of the present work is the theory of thermal explosion of self-accelerating reactions under isothermal conditions, the authors' concept (Ref. 4) of the existence of quasi-steady thermal conditions in the course of reaction prior to explosion being the basis of their study. N. N. Semenov's diagram for self-accelerating reactions, which shows the quasi-steady course of reaction, is studied, and then the authors discuss and apply the quasi-steady theory of autocatalytic reactions of first order proceeding with constant parameters of the system. It is shown

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04040

The Quasi-steady Theory of Thermal Explosion S/076/60/034/010/008/022
of Self-accelerating Reactions B015/B064

that under quasi-steady conditions the rate of heat accumulation is much lower than the rate of heat evolution; thus, it is proved that the former may be neglected, and that only the process prior to explosion proceeds in a quasi-steady manner. It is mathematically proved that under quasi-steady conditions the rate of heat accumulation is determined by the reaction acceleration. The proof of the existence of quasi-steady conditions and the definition of the criterion for the quasi-steady state indicates that below the limit of spontaneous ignition, all reactions proceed in a quasi-steady manner, and that also the process prior to explosion is quasi-steady near the limit. A system of equations for quasi-steady conditions is solved, a scheme for determining the characteristics (of the quasi-steady course of the thermal explosion above and below the limit) of thermal explosion is given for self-accelerating reactions. Highly self-accelerating reactions (isothermal approximation) and thermal explosion of condensed explosives are also subject of this paper. The authors thank Academician N.N.Semenov, Academician Ya.B. Zel'dovich, and Professor D.A. Frank-Kamenetskiy for their interest in this work, and their helpful advice. There are 6 figures, 3 tables, and 9 Soviet references.

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84628

The Quasi-steady Theory of Thermal
Explosion of Self-accelerating Reactions

S/076/60/034/010/008/022
B015/B064

ASSOCIATION: Akademiya nauk SSSR Institut khimicheskoy fiziki Moskva
(Academy of Sciences USSR, Institute of Chemical Physics,
Moscow)

SUBMITTED: January 17, 1959

X

Card 3/3

Dubovitskiy, F.I.

81867

8/020/60/133/02/42/068
B004/B064

11.1000

AUTHORS: Manelis, G. B., Merzhanov, A. G., Dubovitskiy, F. I.

TITLE: On the Problem of the Mechanism of Powder Burning 1

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 2,
pp. 399 - 400

TEXT: Proceeding from experiments conducted by P. F. Pokhil (Ref. 1) the authors investigated whether the burning of dispersed powder particles occurs in the hot flame zone near the maximum temperature, or whether its decomposition occurs already on the surface of the powder. For this purpose an isothermal estimation of the lifetime t_{life} of a particle is carried out. It was assumed that the decomposition of the particles starts at T_{surf} of the surface. Equations are written down for the burning rate u , for t_{life} , and for x_{disp} , the path of the dispersed particles. T_{surf} , t_{life} , x_{disp} were calculated on the basis of the experimentally found values for u , and x_{disp} compared with the

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On the Problem of the Mechanism of Powder
Burning

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S/020/60/133/02/42/068
B004/B064

experimental value x_{gas} of the breadth of the dark zone in front of the flame. The data for pyroxiline powder is given in Table 1. The following conclusions are drawn: An exothermal decomposition occurs in the condensed phase, causing the dispersion of a considerable part of the powder. The decomposition of the dispersed particles occurs close to the surface of the burning powder with 300 cal/g and more being released. The final reaction occurs with the formation of the final products, and release of the rest of the heat in the zone of maximum temperature. There are 1 table and 6 references: 4 Soviet and 2 American.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR
(Institute of Chemical Physics of the Academy of
Sciences, USSR)

PRESENTED: March 2, 1960, by V. N. Dondrat'yev, Academician

SUBMITTED: February 27, 1960

Card 2/2

4

89572

S/076/61/035/002/006/015

B124/B201

11.8200

AUTHORS: Dubovitskiy, F. I., Strunin, V. A., Manelis, G. B., and
Merzhanov, A. G.

TITLE: Thermal decomposition of tetryl at varying m/V values

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 2, 1961, 306-313

TEXT: A. Lukin and S. Z. Roginskiy (Ref. 5: Acta chem.-phys. USSR, 2, 8, 1935) found a critical ratio to exist between the weight m and the volume V of the reaction vessel in tetryl (2,4,6-trinitro phenyl methyl nitramine), in which the slow decomposition passes over into an explosion under the promoting action of various additions (NO₂ et al.). An extensive study has been made of the kinetic rules governing the isothermal decomposition of molten tetryl as a function of the m/V ratio. The reaction concerned was examined in a device made from stainless steel, as diagrammatically shown in Fig. 1. The pressure rise was measured with the aid of a thin membrane made of stainless steel to which transducer 5 was fastened. The change of resistance of 5 was determined by a PПЗ-2 (GPZ-2)

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Thermal decomposition of tetryl...

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B124/B201

galvanometer inserted into the diagonal of the bridge. The measurement was made by the compensation principle. The membrane was brought back to zero position by introducing nitrogen from bomb 6 into the compensator. The pressure rise was measured at given time intervals with the pressure gauges 7 and 8 connected to the compensator. Also a strain gauge was fastened onto the membrane, to serve as second arm of the bridge and for a compensation of temperature fluctuations. The clamp 4 (Fig. 2) was pressed onto sealings made of fluorine-containing synthetic material 3 between flanges 1 and 5, the tubes from the strain gauge were via tube 6 connected to the outer arms of the bridge. The minimum measurable pressure is 0.1 mm Hg, the reading accuracy on the mercury manometer ± 0.2 mm Hg. The gaseous products were analyzed for NO_2 , NO, N_2O , CO, and CO_2 .

Samples were taken by means of traps 9 and 10 (Fig. 1) and cuvette 11. The kinetic curves of gas evolution at 150°C (Fig. 3) and 160°C (Fig. 4) in the coordinates: conversion degree η - time at various m/V values are given. The m/V maximum was about 44 times as large as the corresponding minimum; the maximum end pressure of the decomposition products was about 6000 mm Hg. The curves show that the reaction kinetics is practically independent of the mass of the substance, and that the decomposition

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S/076/61/035/002/006/015

B124/B201

Thermal decomposition of tetryl...

rate increases at all temperatures with rising m/V . The percent content of NO_2 , NO , and condensation products drops with increasing decomposition, while the percentage of CO_2 and N_2 increases somewhat toward the end of the reaction, and the CO content remains practically unchanged (Table 1). The change in the number of NO_2 and NO moles per mole of tetryl as a function of the conversion degree for various m/V at 150°C is given; k_1 is the constant of the monomolecular reaction, k_2' that of the autocatalytic reaction, and k_3 is a constant depending on m/V , in which connection $d\eta/dt = k_1(1 - \eta) + k_2'\eta(1 - \eta) + k_3\eta(1 - \eta) = k_1(1 - \eta) + k_2(1 - \eta)$, where $k_2 = k_2' + k_3$. The dependence of k_1 on m/V is shown in Fig. 7. The initial acceleration of the reaction is correlated with the course of the macroscopic stage of the reaction, which leads to the formation of a highly volatile product with a catalytic action. This process is inhibited after some time by the tetryl decomposition. The further acceleration does not depend on the volume of the reaction vessel, which is indicative of an autocatalysis by the final condensation products

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B124/B201

Thermal decomposition of tetryl...

(picric acid according to Hinshelwood). The effective values of the activation energy and of the factor of the exponential function in the Arrhenius equation were calculated from the rate constants (Table 3), the values obtained for k_1 being characteristic of the monomolecular decomposition,

whereas an activation energy of 37 kcal/mole was found for k_2 with all m/v.

The explanation offered by the authors fits the respective hypothesis by N. M. Emanuel' (Ref. 10: Makroskopicheskiye stadii, osobaya rol' nachal'nogo perioda i mekhanizm deystviya ingibitorov i polozhitel'nykh katalizatorov v tsepnykh reaktsiyakh (Macroscopic stages, special role of the initial period and mechanism of the action of inhibitors and positive catalysts in chain reactions); Collection: "Voprosy khimicheskoy kinetiki, kataliza i reaktsionnoy sposobnosti" ("Problems of chemical kinetics, catalysis and reactivity"), Moscow, 1955, p. 117) on the significant role of the initial initiating stage. There are 9 figures, 3 tables, and 10 references: 4 Soviet-bloc and 6 non-Soviet-bloc. The references to the English language publications read as follows: M. A. Cook, M. J. Abegg, Industr.a.Engng. Chem. 48, 1090, 1956.

Card 4/14 Inst. Chem Physics AS USSR

S/076/61/035/003/004/023
B121/B203

// 2216

AUTHORS: Dubovitskiy, F. I., Manelis, G. B., and Smirnov, L. P.
TITLE: Kinetics of thermal decomposition of trinitrophenyl methyl
nitramine (tetryl)
PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 3, 1961, 521-529

TEXT: The authors studied the kinetics of thermal decomposition of trinitrophenyl methyl nitramine (tetryl) with exact analysis of the decomposition products. They recorded the kinetic curves for the gas generation occurring in the decomposition of tetryl at temperatures between 140.3 and 164.9°C. The nitric oxide content in the gaseous phase increases slightly at the beginning of decomposition, and then remains constant. The carbon monoxide and carbon dioxide contents increase at the end of the reaction. An increase in the reaction temperature increases the nitric oxide and nitrogen dioxide contents. The kinetic curves for the accumulation of N₂, CO, CO₂, and NO are S-shaped. An analysis of the condensed decomposition products of tetryl shows that the condensed phase contains, besides picric acid, considerable amounts of 2, 4, 6-trinitro-anisole and N-methyl-2, 4, 6-tri-
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8/076/61/035/003/004/023
B121/B203

Kinetics of ...

nitro-aniline. A chromatographic method was developed for the quantitative determination of condensed products. The products were applied to silica gel dyed with rhodamine-6-Zh. The separately isolated products were spectroscopically investigated in alcoholic solution in the ultraviolet spectral range. To distinguish 2, 4, 6-trinitro-aniline from its N-alkyl derivatives, the infrared spectra were also taken with an MKC-11 (IKS-11) spectrophotometer with LiF prism in the range of 2.85-3.2 μ . After the separation, the condensed decomposition products were hydrolyzed to picric acid, the quantitative determination of which was performed with an C Φ -4 (SF-4) spectrophotometer. The kinetic curves for the accumulation of 2, 4, 6-trinitro-anisole and picric acid, as well as for the consumption of tetryl, are S-shaped. The formation of N-methyl-2, 4, 6-trinitro-aniline proceeds very rapidly at the beginning of the reaction, and slows down later. An addition of picric acid was found to accelerate the tetryl decomposition, the picric acid acting as a catalyst with acid-basic character. There are 6 figures, 5 tables, and 10 references: 4 Soviet-bloc and 6 non-Soviet-bloc. The four references to English-language publications read as follows: R. C. Farmer, J. Chem. Soc., 117, 1603, 1920; C. N. Hinschelwood, J. Chem. Soc., 119, 721, 1921; E. Lederer, Chromatography, Amsterdam - Houston -

Card 2/3

Kinetica of ...

8/076/6. /035/003/004/723
B121/B203

London - New York, 1953, p. 44; W. A. Schroeder, P. E. Wilcox, K. N. Trueblood, A. O. Dekker, *Analyt. Chem.*, 23, 1740, 1951.

ASSOCIATION: Akademiya nauk SSSR Institut khimicheskoy fiziki (Academy of Sciences USSR, Institute of Chemical Physics)

SUBMITTED: May 21, 1959

Card 3/3

11.6300
26.5200

27683
S/076/31/035/009/008/015
B106/B110

AUTHORS: Merzhanov, A. G., Barsykin, V. V., Abramov, V. G., and
Dubovitskiy, P. I.

TITLE: Thermal explosion in the liquid phase under conditions of a
purely convective heat transfer

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 9, 1961, 2083 - 2089

TEXT: The authors tried to realize the thermal explosion of explosives in the liquid phase for the limiting case of purely convective heat transfer. The heat exchange is of such intensity that no temperature distribution takes place in the reaction zone, and the total temperature gradient falls to the wall of the reaction vessel. Such a heat exchange may be achieved by intensive artificial intermixing of the substance. Under these conditions, the heat-transfer coefficient from the reaction zone to the ambient medium may easily be measured since it is derived from the heat-transfer coefficient through the wall of the vessel. Moreover, these conditions may serve as starting point for a detailed study of the complicated convective heat transfer. Two explosives with strongly different

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S/075/61/035/009/008/015

Thermal explosion in the liquid phase ...

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properties were chosen for the experiments: Dina (dinitrooxydiethyl-nitramine; melting point 52.5°C) and Tetryl (melting point $\approx 130^{\circ}\text{C}$). The decomposition of Dina is a reaction of first order and only leaves a small condensed residue. The rate of heat development per unit volume is independent of the extent of transformation, and is only determined by the temperature. Under the conditions of a purely convective heat transfer, Dina represents, therefore, the simplest example for the theory of thermal explosion according to N. S. Semenov (Ref. 7: Zh, Uspekhi fiz. nauk, RPKhO, 60, 241, 1928; 23, 251 1940). On the other hand, the decomposition of Tetryl has an autocatalytic course and leaves a very large condensed residue. Tetryl is a good example for the quasisteady theory of thermal explosion developed by the authors (Ref. 6: A. G. Merzhanov, F. I. Dubovitskiy, Dokl. AN SSSR, 124, 362, 1959; Ref. 9: same authors, Dokl. AN SSSR, 120, 1068, 1958; Zh. fiz. khimii, 34, 2235, 1960). The investigation method had been elaborated previously (Ref. 2: A. G. Merzhanov, V. G. Abramov, F. I. Dubovitskiy, Dokl. AN SSSR, 128, 1238, 1959) and was only completed by a device for the intermixing of the substance. This method permits a determination of all fundamental characteristics of thermal explosion. In Table 1, the experimental results

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Thermal explosion in the liquid phase ...

S/076/51/035/009/008/015
B106/B110

on the thermal explosion of Dina are compared with the values calculated according to Semenov's theory; they agree well. The data for the calculations were obtained independently of the experiments. Table 2 gives a comparison of results of experimental investigation of the thermal explosion of Tetryl with the critical temperature and heating calculated by means of the equations derived in Ref. 6 and Ref. 9. Also in this case, the agreement is good. D. A. Frank-Kamenetskiy (Ref. 1: Diffuziya i teploperedacha v khimicheskoy kinetike (Diffusion and heat transfer in chemical kinetics), M.-L., 1947) is mentioned. There are 2 figures, 2 tables, and 9 references: 7 Soviet and 2 non-Soviet-bloc. The two references to English-language publications read as follows: A. J. B. Robertson, Third Symposium on Combustion, 1949, 545; W. G. Chute, K. G. Herring, L. E. Toombs, C. F. Wright, Canad. J. Res., B26, 89, 1948.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki
(Academy of Sciences USSR, Institute of Chemical Physics)

SUBMITTED: February 5, 1960

Card 3/5

35060

S/195/62/003/001/001/010
E071/E136

// 2715

AUTHORS: Manelis, G.B., Rubtsov, Yu.I., Smirnov, L.P., and
Dubovitskiy, F.I.

TITLE: Kinetics of thermal decomposition of pyroxilin

PERIODICAL: Kinetika i kataliz, v.3, no.1, 1962, 42-48

TEXT: As the literature data on thermal decomposition of nitrocellulose are contradictory, the authors investigated the kinetics of thermal decomposition of pyroxilin powder within a temperature range of 140-165 °C. The kinetics were studied by three different methods: by the evolution of heat in a double calorimeter (in vacuo and at atmospheric pressure); by changes in weight on an automatic thermal balance in the presence of air; and by gas evolution in a static vacuum apparatus with subsequent analysis of gaseous decomposition products. It was found that thermal decomposition of pyroxilin powder in air as well as in vacuo takes place to a certain depth of decomposition (depending on the temperature) with autocatalysis of the first order; subsequently the process continues as the first order reaction. The heat effect of thermal decomposition is

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X

Kinetics of thermal decomposition... S/195/62/003/001/001/010
E071/E136

independent of the temperature and is on average about 750 cal/g which amounts to more than 80% of the heat of combustion (about 900 cal/g). On decomposition in vacuo the heat effect decreases to 515 cal/g. In the autocatalysis equation

$$d\eta/dt = k_1(1 - \eta) + k_2 \cdot \eta(1 - \eta)$$

which describes well this stage of the reaction, k_1 and k_2 were calculated from experimental data. The temperature dependence of these constants (for heat evolution in air) was found to be:

$$k_1 = 10^{19} \cdot e^{-\frac{47000}{RT}} \text{ sec}^{-1},$$

$$k_2 = 10^{12} \cdot e^{-\frac{31000}{RT}} \text{ sec}^{-1}.$$

The main gaseous product in the initial stage of decomposition is NO; with increasing degree of decomposition the percentage of
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Kinetics of thermal decomposition... S/195/62/003/001/001/010
EO71/E136

CO₂ increases and that of NO decreases, indicating that the initially split NO₂ group reacts quickly with the condensed phase leading to the formation of nitrogen oxide, carboxyl and carbonyl groups. The process of decarboxylation proceeds with a lower velocity than the reaction of formation of NO and develops mainly at the end of decomposition when the destruction of the polymeric chain is well advanced. The catalytic influence of gaseous decomposition products is indicated by the fact that the velocity constant k_2 is lower on removal of the gaseous products than it is in their presence. However, the autocatalysis of thermal decomposition of pyroxilin was also observed on continuous removal of gaseous products, indicating that functional groups (carboxyl, carbonyl, etc.) of the polymeric molecules, formed in the course of the reaction, also have a catalytic influence. There are 6 figures and 3 tables.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR
(Institute of Chemical Physics, AS USSR)

SUBMITTED: April 3, 1961

Card 3/3

X

KORSUNSKIY, B. L.; DUBOVITSKIY, P. I.

Kinetics of the thermal decomposition of N, N-dimethylnitroamine.
Dokl. AN SSSR 155 no. 2:402-405 Mr '64. (MIRA 17:5)

1. Institut khimicheskoy fiziki AN SSSR. Predstavleno akademikom
V. N. Kondrat'yevym.

L 06524-67 RT(1)/RT(a)/WP(a) WJ/JW
ACC NR: AP7000871

SOURCE CODE: UR/0074/66/035/004/0656/0683

MERZHANOV, A. G., DUBOVITSKIY, P. I., Institute of Chemical
Physics, Academy of Sciences USSR (Institut Khimicheskoy Fiziki AN SSSR)

"Modern State of the Theory of Thermal Explosion"

"

Moscow, Uspekhi Khimii, Vol 35, No 4, 1966, pp 656-683

Abstract: A survey is presented of the present day state of the theory of thermal explosion and means for its further development. The generalization and development of the classical theory of thermal explosion, including treatments of thermal explosion as one of the systems of ignition, the steady-state theory of thermal explosion, the nonsteady-state theory of thermal explosion, and the quasisteady-state theory of thermal explosion, are discussed. Systems of thermal explosion not described by the classical theory are reviewed: dynamic systems of thermal explosion with heating and cooling, thermal explosion in the presence of conductive heat transfer in the surrounding medium, focal systems of thermal explosion, and hydrodynamic problems of the theory of thermal explosion. Methods of experimental investigation and problems of verifying the theory are discussed, as is the mechanism of thermal explosion in condensed media. In the latter section, the physicochemical aspects of the mechanism of thermal explosion are discussed, including the influence of bulk gas evolution during decomposition upon the

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0923

1178

L 06524-67

ACC NR: AF7000471

occurrence of processes of thermal explosion, the thermal explosion of volatile substances, the thermal explosion of solid organic substances, and thermal explosion in the presence of polymorphic transformations. Orig. art. has: 11 figures, 4 formulas, and 5 tables. [JPRS: 37,17]

TOPIC TAGS: thermal explosion, ignition

SUB CODE: 21/ SUBM DATE: none / ORIG REF: 055 / OTH REF: 020

Card 2/2 LS

DUBOVITSKIY, G., mayor

Calculation of a registration point site. Voen. vest. 43
no.2:78-79 P '64. (MIRA 17:1)

DUBOVITSKIY, I. [Dubovyts'kyi, I.], inzh.

Electrets. Nauka i zhyttia 12 no.11:22, 28 N '62. (MIRA 16:1)
(Electrets)

DUBOVITSKIY, M.A. [deceased]

Prophylactic medical surveys in the city of Tartu [with summary in English]. Vop.onk. 4 no.1:94-96 '58. (MIRA 11:4)

1. Iz Respublikanskogo onkologicheskogo dispensera ESSR (glavnyy vrach - M.A.Dubovitskiy).

(NEOPLASMS, prevention and control,
mass survey (Rus))

DUBOVITSKIY, P. A. (Dubovitskiy, P. A.)

Developing outer wharves. Rech. transp. 16 no. 6:27-28 Jo '97.
(MIRA 10:8)

1. Nachal'nik Ger'kovskogo otdeleniya Giprorechtranca..
(Loading and unloading) (Wharves)

DUBOVITSKIY, P.A., insh.

Greater use of grab cranes for loading stone. Rech. transp. 17
no. 4:33 Ap '57. (MIRA 11:4)
(Cranes, derricks, etc.) (Loading and unloading)

ГЕBOVITSKIY, P.A., insh.

Increase the role of river transportation in servicing the industrial enterprises of the Gorkiy Water Transportation Development. Rech. transp. 18 no.5:18-20 M '59. (MIRA 12:9)
(Gorkiy Province--Inland water transportation)

DUBOVITSKIY, S. V.

Bee Culture

Extension of the nest in spring Pchelovodstvo 29, no. 4, April 1952

9. Monthly List of Russian Accessions, Library of Congress, August ²195~~7~~, Uncl.

5 (4)

AUTHORS:

Kesmeyanov, A. N., Nogina, O. V.,
Dubovitskiy, V. A.

SOV/62-59-8-32/42

TITLE:

Effect of the Time Factor on the Degree of Association of
Titanium Alkoxy Derivatives in a Benzene Solution

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 8, pp 1496-1498 (USSR)

ABSTRACT:

This brief survey discusses the property dealt with in numerous papers (Refs 1-3) of the alkoxy derivatives of titanium to associate in aqueous benzene solutions. It has been shown that the methods used for the determination of the molecular weight (kryoscopy and ebullioscopy) yielded a higher molecular weight than corresponded to the monomer. The authors of the present paper now succeeded in showing that the degree of association of

the substances: $(RO)_4Ti$, $ClTi(OR)_3$, $(RO)_2TiO$, $\begin{matrix} Cl \\ \diagup \\ TiO, \\ \diagdown \\ RO \end{matrix}$, $\begin{matrix} Cl \\ \diagup \\ TiO \cdot ROH, \\ \diagdown \\ RO \end{matrix}$
 $Cl_2TiO \cdot 2ROH$ changes gradually. It diminishes and, after some

hours, equals 1. The decomposition rate of the associates, however, is not high, while the activation energy of the

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Effect of the Time Factor on the Degree of Association SOV/62-59-8-32/42
of Titanium Alkoxyl Derivatives in a Benzene Solution

dissociation of the associates is considerable. Figures 1 and 2 show the change in molecular weight of some of the relevant substances in the course of time. The table contains the molecular weights of the substances under investigation. Some substances had been synthesized by the authors for the purposes of this paper and had actually been obtained for the first time. It was seen from the curves that initial monomers are formed by dissociation. Thus it is possible to use kryoscopy for the determination of the molecular weights of the compounds under investigation. The authors will report on the newly synthesized substances in future papers. There are 3 figures, 1 table, and 5 references, 1 of which is Soviet.

ASSOCIATION: Institut elementorganicheskikh soedineniy Akademii nauk SSSR
 (Institute of Elemental-organic Compounds of the Academy of
 Sciences, USSR)

SUBMITTED: February 18, 1959

Card 2/2

5(3)

SOV/79-29-9-2/76

AUTHORS:

Nesmeyanov, A. N., Lutsenko, I. F., Khomutov, R. M., Dubovitskiy, V. A.

TITLE:

Vinyl Esters of Sulfonic Acids

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 9,
pp 2817 - 2820 (USSR)

ABSTRACT:

To synthesize the vinyl esters of various carboxylic acids the authors made use of the reaction of acid halides of carboxylic acids with halogenmercury acetaldehyde or halogeno mercury ketones, the only reaction products being the acetates of the enol forms of oxo compounds (Refs 1,2). The said reaction did not always exhibit the same character: thus, for example, the chloro carbonic acid ester, the acid chlorides of sulfonic acids, and silicon tetrachloride did not react with the halogeno mercury oxo compounds. Mercury bisacetaldehyde $Hg(CH_2CHO)_2$ (Ref 3) synthesized by the authors, proved to be more reactive as compared with the above aldehydes: this permitted the acid chlorides of the sulfonic acids to be introduced into the reaction according to the following

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Vinyl Esters of Sulfonic Acids

SOV/79-29-9-2/76

scheme:



Chloro mercury acetaldehyde did not react any more. Mercury bisketones reacted in the same manner. To prevent the vinyl ester of sulfonic acid from polymerizing, pyridine must be added, and the mercury salts must be removed from the reaction solution. By complying with these prudential measures, the vinyl esters of methane- and ethane sulfonic acid were obtained in yields of 45 or 47%. The yields of vinyl esters of benzene- and p-toluene sulfonic acid amounted to 70 and 75% correspondingly. Reaction of thionyl chloride with mercury bisacetaldehyde yielded divinyl sulfite (45%); when applying sulfuryl chloride it cleaved and developed SO_2 , without any

resulting divinyl sulfate. Reaction of vinyl ester of benzene sulfonic acid with benzoyl chloride according to A. Sieglitz and O. Horn (Ref 4) gave a high yield of β, β -dichloropropiophenone according to the suggested scheme 2. The inter-

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Vinyl Esters of Sulfonic Acids

SOV/79-29-9-2/76

mediate product α -chloro- β -benzoyl ethyl-p-toluene sulfonate separated by this reaction was completely transferred into β, β -dichloro propiophenone with the equivalent amount $AlCl_3$; this confirms the above reaction course. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: January 8, 1959

Card 3/3

66174

SOV/20-128-5-20/67

~~5(2,3)~~ 5.3700(B)

AUTHORS: Nesmeyanov, A. N., Academician, Nogina, O. V., Dubovitskiy, V. A.

TITLE: Activation Energy of the Disaggregation Process of Associated Titanium Alkoxy Derivatives

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 5, pp 964 - 965 (USSR)

ABSTRACT: The association degree of these derivatives decreases comparatively slowly in diluted benzene solutions. Within several hours all associates disappear (Ref 1). The association of these derivatives is explained by intermolecular coordination bonds between the oxygen atoms of one molecule and the titanium atoms of the adjacent molecules. (Refs 2-5). The dependence of this phenomenon on temperature was investigated and the activation energy of disaggregation determined in this paper. The method of cryoscopy was used for this purpose. Figure 1 shows the kinetic curves of the disaggregation process of the associates of tetra-n-propoxy titanium at various temperatures. The values of activation energy were computed from the dependencies of the initial velocities on temperature (Fig 2). They are 7.7 kcal/mol for tetra-n-propoxy titanium, 8.0 kcal/mol ✓

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Activation Energy of the Disaggregation Process of
Associated Titanium Alkoxy Derivatives

66174

SOV/20-128-5-28/67

for associated tetraethoxy titanium, and 8.1 kcal/mol for di-n-propoxy titanium oxide. Limit concentration at which the association degree of titanium alkoxy derivatives decreases to 1 depends little on the structure of the titanium compound (Fig 3). The structure of the alkyl, however, has a distinct effect on this phenomenon. Spatial obstacles influence the association degree of the titanium derivatives mentioned. Association does not take place at all if there is a ramified carbon chain of tetraalkoxy titanium at the carbon atom adjacent to titanium (tetraisopropoxy titanium, tetratertiary butoxy titanium, references 2,6) in the case of concentrations of benzene solutions up to 2.0 mol%. If the ramification of the alkyl chain in tetraalkoxy titanium occurs on the β -carbon atom, the tetraalkoxy titaniums are associated in benzene solutions. Also in this case the association degree decreases gradually and reaches 1 after several hours. There are 3 figures, and 6 references, 1 of which is Soviet.

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Activation Energy of the Disaggregation Process of
Associated Titanium Alkoxy Derivatives

66174
SOV/20-128-5-20/67

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the Academy
of Sciences, USSR)

SUBMITTED: July 9, 1959

4

Card 3/3

81673

S.3700

2209, 1318, 1312 only

8/020/60/134/006/018/031
B016/B067

AUTHORS: Nesmeyanov, A. N., Academician, Negin, O. V., and
Dubovitskiy, V. A.

TITLE: Slow Dissociation of the Associates of the Alkoxyl and
Alkyl Derivatives of Metals in Solutions

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 134, No. 6,
pp. 1363-1366

TEXT: In earlier papers (Refs. 1,2) the authors described the slow dis-
integration of associates of the alkoxyl titanium derivatives in dilute
benzolic solutions. In the present investigation they observed that the
phenomenon occurs also in the solutions of organic compounds of other
metals. It was found that the degree of association in the alkoxyl
derivatives of tin, zirconium, and aluminum cryoscopically determined
decreases with time and that within some hours it becomes equal to one.
Fig. 1 shows the curves of the variation with time in the molecular
weights of $(n-C_3H_7O)_4Sn$ in benzolic solution with a concentration of

X

Card 1/3

84673

Slow Dissociation of the Associates of the
Alkoxy and Alkyl Derivatives of Metals
in Solutions

S/020/60/134/006/018/031
B016/B067

0.100 mol% (Curve 1) and an analogous curve (2) for $(n-C_4H_9O)_4Zr$ (concentration 0.161 mol%). The production method of tetra-n-propoxy-tin and of tetra-n-butoxy-zirconium (Refs. 4,5) and of other products used is described. Fig. 2 gives the analogous curves (1,2,3) for $(iso-C_4H_9)_2AlOC_2H_5$ in benzolic solution (concentration 0.099 mol%) and for $(n-C_3H_7O)_3Al$ as well as for $(iso-C_4H_9O)_3Al$. The authors state that at constant concentration and temperature the dimer of triethyl aluminum in dilute benzolic solution slowly dissociates to the monomer stage. Fig. 3 shows a curve similar to those already obtained for $(C_2H_5)_3Al$, and Fig. 4 shows a curve for $(n-C_4H_9O)_4Ti$ (1) in nitrobenzolic solution as well as (2) for $(n-C_3H_7O)_4Ti$ in dioxane solution. Curve (3) illustrates the variation in the molecular weight of tetra-n-propoxy-titanium dissolved in cyclohexane. There are 4 figures and 23 references: 7 Soviet, 7 US, 2 French, 3 German, and 4 British.

Card 2/3

84673

Slow Dissociation of the Associates of the
Alkoxy and Alkyl Derivatives of Metals
in Solutions

S/020/60/134/006/018/031
B016/B067

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii
nauk SSSR (Institute of Elemental-organic Compounds of
the Academy of Sciences, USSR)

SUBMITTED: July 12, 1960

Card 3/3

20938

5 3700

2209, 1164

S/062/61/000/003/004/013
B117/B208AUTHORS: Nesmeyanov, A. N., Nogina, O. V., and Dubovitskiy, V. A.

TITLE: Synthesis of dialkoxo (aryloxy) titanium oxides by ester interchange of di-n-propoxy-titanium oxide

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no. 3, 1961, 437-441

TEXT: The authors outlined the possibility of obtaining dialkoxo (aryloxy) titanium oxides and bis(triethyl-siloxy)titanium oxide by ester interchange of the easily accessible di-n-propoxy titanium oxide. $(C_2H_5O)_2TiO$ and $(1-C_5H_{11}O)_2TiO$, $(n-C_6H_{13}O)_2TiO$, $(C_6H_5O)_2TiO$, $[(C_2H_5)_3SiO]TiO$, hitherto not yet described, were prepared in this way. Diphenoxo titanium oxide was also prepared in the form of its molecular compound with phenol. All experiments were carried out with completely dry raw materials under exclusion of atmospheric moisture. The ultrared spectra of these compounds were obtained on a double-beam UR-spectrophotometer. The spectra were taken of solutions of the substances in carbon disulfide and carbon tetra-

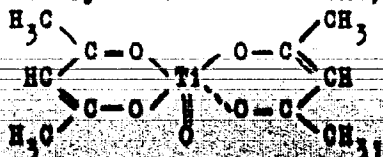
Card 1/3

20938

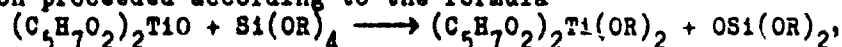
Synthesis of dialkoxy (aryloxy)...

S/062/61/000/003/004/013
B117/B208

chloride, as well as of a paste in vaselin oil. But no characteristic frequencies were found in the range of 600-1400 cm^{-1} that could be assigned to the $\text{Ti}=\text{O}$ bond. Also titanium oxide bis-acetylacetonate was prepared by reaction of di-n-propoxy titanium oxide with acetylacetonone. This compound was prepared by hydrolysis by A. Jazamoto, S. Kambara (see below) who have assigned it a cyclic dimeric structure. Cryoscopic determination of the molecular weight of titanium oxide bis-acetylacetonate showed, contrary to this statement, that this compound has obviously the structure



and is a monomer in dilute solutions. The attempt of carrying out the addition to the $\text{Ti}=\text{O}$ double bond in titanium oxide bis-acetylacetonate gave no addition product but dialkoxy titanium bis-acetylacetonate. Thus, the reaction proceeded according to the formula



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Synthesis of dialkoxo (aryloxy)...

S/062/61/000/003/004/013
B117/B208

where $R = C_2H_5$; $n-C_3H_7$. The authors thank L. A. Kazitsyna and G. A. Rudenko of the Moskovskiy gosudarstvennyy universitet (Moscow State University) for determining the IR spectra of di-n-propoxy titanium oxide samples. N. A. Chumayevskiy is thanked for taking the IR spectra of the remaining compounds, which was done at the laboratoriya akad. I. V. Obreimova (Laboratory of Academician I. V. Obreimov) of the authors' association. There are 5 figures and 6 references: 5 Soviet-bloc and 3 non-Soviet-bloc. The reference to the English-language publication reads as follows: A. Jamancto, S. Kambara, J. Amer. Chem. Soc. 79, 4344, 1957.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds, Academy of Sciences USSR)

SUBMITTED: January 8, 1960

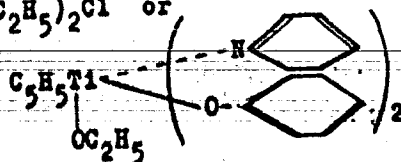
X

Card 3/3

S/062/62/000/008/013/016
B101/B180

AUTHORS: Nesmeyanov, A. M., Nogina, O. V., and Dubovitskiy, V. A.
TITLE: Data on the titanium - cyclopentadienyl ring bond in
 $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$
PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 8, 1962, 1481-1483

TEXT: Using the method of A. K. Fischer, G. Wilkinson (J. Inorg. and
Nucl. Chem. 2, 149, (1956)) the ionic nature of the Ti bond in sandwich
compounds was checked by reaction with $FeCl_2$ or $Fe(II)$ acetyl acetate,
in argon atmosphere, and tetrahydrofuran solvent at $65^\circ C$. Results:
(1) no ferrocene is formed from $(C_5H_5)_2TiCl_2$, $(C_5H_5)_2Ti(C_6H_5)_2$, $C_5H_5TiCl_3$,
 $C_5H_5Ti(OC_2H_5)Cl_2$, $C_5H_5Ti(OC_2H_5)_2Cl$ or



Card 1/2

Data on the titanium - ...

S/062/62/000/008/013/016
B101/B180

(synthesized for the first time, report printing). (2) ferrocene is formed from $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$. (3) the ionic nature of the bond in $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$ was further demonstrated by the ease with which these compounds hydrolyze in the presence of water at 60-80°C. (4) The compound $C_5H_5Ti(OC_2H_5)_2Cl$ was synthesized for the first time by reaction between CH_3COCl and $C_5H_5Ti(OC_2H_5)_3$; b.p. 113-114°C/0.5 mm Hg, n_D^{20} 1.5812, d_4^{20} 1.2253. There are 2 tables. ✓

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: February 17, 1962

Card 2/2

NESMEYANOV, A. M.; MOGINA, O. V.; DUBOVITSKIY, V. A.

Alkylation of bis-(cyclopentadienyl) titanium dichloride by
means of acetyl chloride. Izv. AN SSSR Otd. khim. nauk no.12:
2254-2255 B '62. (MIRA 16:1)

1. Institut elementoorganicheskikh soedineniy AN SSSR.

(Titanium compounds) (Acetyl chloride)

KESMEYANOV, A.N.; NOGINA, O.V.; SURIKOVA, T.P.; DUBOVITSKIY, V.A.

Preliminary report on the alkylation of bis(cyclopentadienyl)titanium dichloride is erroneous. Izv. AN SSSR. Ser.khim. no.9:1699 S '63. (MIRA 16:9)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Titanium compounds) (Cyclopentadiene)

... involved for reaction with dihenaryisocyclopentadiene (isolated in a ...
... brominating to form titanocene dibromide and the dibromide of a ...
... 1,3,5,6,7,8-tetrahenarybutadiene ...

DVORYANTSEVA, G.G.; SHEYNTER, Yu.N.; NESMEYANOV, A.N., akademik; NOGINA, O.V.;
LAZAREVA, N.A.; DOBOVITSKIY, V.A.

Infrared spectra of some cyclopentadienyl compounds of titanium.
Dokl. AN SSSR 161 no.3:603-606 Mr '65.

(MIRA 18:4)

1. Institut elementoorganicheskikh soyedineniy AN SSSR i Institut
khimii prirodnykh soyedineniy AN SSSR.

NESMEYANOV, A.N., akademik; DUBOVITSKIY, V.A.; NOGINA, O.V.; BOCHKAREV, V.N.

Mass spectra of some monocyclopentadienyl derivatives of titanium.
Dokl. AN SSSR 165 no.1:125-126 N '65.

(MIRA 18:10)

1. Institut elementoorganicheskikh soyedineniy AN SSSR i Institut
khimii prirodnikh soyedineniy AN SSSR.

... (Academician), Fedin, ...
... (Academician), Lazareva, N. S.

... clear magnetic resonance with
... allyl hopping in the cyclopentadiene

... study, v. 161, no. 3, 1965, p.

... titanium, cyclopentadiene,

... of chlorine atoms in the complex

... 2662
... 59
... 49
... 2

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... at 50 m² with ... stabilization. ...
... internal standard. The ...
... Ability of cyclopentadiene ...
... with Fe²⁺ correlates with ...
... The greater the electron ...
... the easier is the formation of ...

1974-12

... is reflected in ...
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... of the ethoxy group. The ...
... is supported by ...
... and $\gamma(\text{OC}_2\text{H}_5)$ are ...
... The authors thank ...
... for measurement of ...
... and 1 figure.

... elementoorganicheskii soyuz ...
... elemental compounds Academy of Sciences ...
... Institut Khimicheskogo Volokna ...
... (Moscow, U.S.S.R.)

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ENCLOSURE

07-21-100

ACC NR: AP6032280

An increase in the wall surface area of the reaction vessel by insertion of capillaries into the reaction chamber increased the initial pressure rise at a rate increasing with time (see Fig. 1). The maximum pressure rise rate for all three isomers occurred at 30–50% decomposition, at which point the degree of autoacceleration (defined as the ratio maximum rate/initial rate) was 5–6. The total amount of gas formed on decomposition was 3.2 mol for the ortho isomer and about 3 mol for the meta and para isomers per mol dinitrobenzene. An increase in the dinitrobenzene vapor concentration within the range 50–800 mm Hg increased the initial and the maximum rate substantially and caused the $p(t)$ curve to assume a saturation character (see Fig. 1). However, the role of the wall reaction in the absence of capillaries apparently was not so great as to markedly change the homogeneous decomposition kinetics. Thus a 10–20-fold increase in the wall surface area caused only a 4–6-fold increase in the initial decomposition rate of the ortho and para isomers. The effect of temperature on the initial decomposition rate of the three isomers was studied under conditions which virtually exclude reaction at the wall. The closeness of the activation energies found for the three isomers suggested that their decomposition mechanism is the same; it apparently consists of the rupture of the C-NO₂ bond. The initial decomposition rate at 350°C of the ortho isomer was 6–7 times as high as that of the meta and para isomers, which decompose at almost the same rate. The corresponding preexponential factor in the Arrhenius equation were $10^{14.6}$, $10^{13.0}$ and $10^{13.5}$ sec⁻¹, respectively. The paper was presented by Academician N. N. Semenov, 7 Jan 66. Orig. art. has: 4 figures and 1 table. [WA-68]

ACC NR: AP6032280

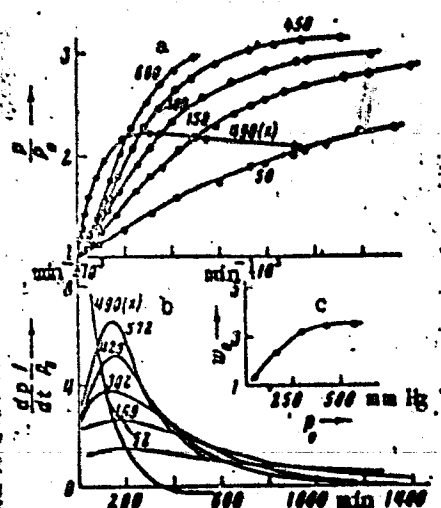


Fig. 1 . Effect of concentration on the gas phase decomposition of o-dinitrobenzene at 340C

a - Gas evolution versus time; b - gas evolution rate versus time; c - initial reaction rate versus initial concentration. Numbers on curves indicate initial pressure in mm Hg. In the experiment indicated with symbol (X) wall surface area was increased 10—20-fold by insertion of capillaries.

SUB CODE: 207, 21/ SUBM DATE: 07Jan66/ ORIG REF: 003/ OTN REF: 003

Card 3/3